A RATIONAL MODEL FOR DISSOLVED OXYGEN IN STREAMS

By

CHANDRA SHEKHAR TRIVEDI

DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
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A Thesis Submitted
In Partial Fulfilment of the requirements
for the Degree of
MASTER OF TECHNOLOGY
IN
CIVIL ENGINEERING

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CERTIFICATES

This is to certify that the work presented in this thesis has been carried out by Shri Chandra Shekher Trivedi, under my supervision and has not been submitted elsewhere for a degree.

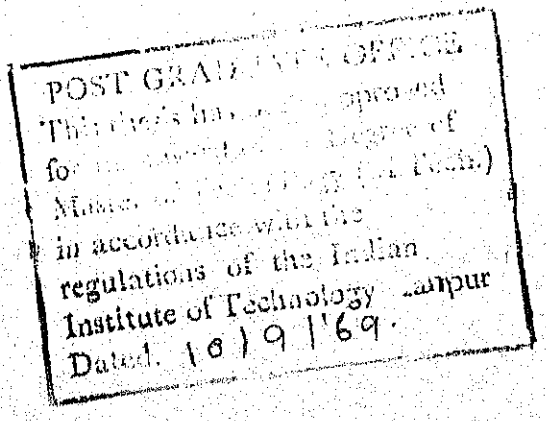
R H Siddiqi

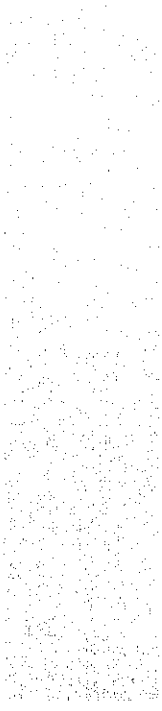
(Dr. R. H. Siddiqi)
Department of Civil Engineering
Indian Institute of Technology
Kanpur

This thesis has been approved for the award of the Degree of Master of Technology in Civil Engineering in accordance with the regulations of the Indian Institute of Technology, Kanpur.

R H Siddiqi

(Dr. R. H. Siddiqi)
Department of Civil Engineering
Indian Institute of Technology
Kanpur





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A second order model for prediction of dissolved oxygen in a polluted stream has been investigated in this study. This model uses Monod's expression for the consumption of organic matter, based on Michaelis Menton hypothesis, to give the microbial concentration in a system, its due consideration. The resulting equation has been solved numerically on IBM 7044/1401 digital computer system using Fortran IV language and the results compared with the experimental data obtained on a simulated plug flow type stream. The values have also been calculated by the Streeter-Phelps first order model for dissolved oxygen for comparison.

The study shows that the model proposed here gives a better approximation to experimental data and hence should better be used for accurate work.

TABLE OF SYMBOLS

t = Time, hours

S = Substrate concentration at any instant, mg/l

X = microbial concentration at any instant, mg/l

S_o = Initial substrate concentration (at t=0), mg/l

X_o = Initial microbial concentration (at t=0), mg/l

μ = Growth rate constant, hr^{-1}

μ_{max} = Maximum value of the growth rate constant, hr^{-1}

K_s = Mechaelis - Menton constant

K_x = Substrate consumed per unit mass of microbial mass synthesised or reciprocal of the yield coefficient, $Y_{x/s}$.

K_1 = B.O.D. reaction rate constant in Streeter - Phelp's mono-molecular formulation, $hour^{-1}$

K_2 = Reaeration rate constant, hr^{-1}

Ke = Endogenous death rate, hr^{-1}

K' = Ultimate oxygen demand per unit mass of substrate (glucose) metabolised, mg O_2/mg glucose as C.O.D.

K" = Ultimate oxygen demand per unit mass of microbial mass metabolised endogenously, mg O_2/mg microbial mass.

C = D.O. concentration at any instant, mg/l

C_s = Saturation D.O. concentration under the existing physical conditions, mg/l.

D = D.O. deficit, mg/l.

CHAPTER I

INTRODUCTION

1.1 GENERAL:

The dissolved oxygen content of a stream, in a nutshell, expresses its conditions and usefulness from the point of view of human and animal consumption, industrial uses and also from the viewpoint of the aquatic life. Oxygen is a gas very sparingly soluble in water, dissolving to the extent of only about 8.4 mg/l at normal temperatures ($25^{o}C$) at the saturation level. Upon this meagre content of the dissolved oxygen, depend the trillions and zillions of the forms of aerobic aquatic life, present in a stream, or anyother water body, to keep themselves alive. Any substantial reduction, therefore, in this vital ingradient to sustain aerobic aquatic life, already in short supply, can cause breaks in the natural food chain, resulting in an upset in the otherwise existing balance of the mixed nature of the aquatic life. This may lead to extinction by death or migrating of certain aquatic creatures (1), which for example, in the case of edible fish and crabs may mean an economic loss, in terms of their food value, for the community dwelling on the banks of the stream. A stream, low in its dissolved oxygen content also becomes unhealthy in its looks and gives rise to obnoxious odors. Its water becomes dark in colour due to the present of the products of anaerobic decomposition of the organic pollutants, and loses its value, both recreational and as a source of water supply.

The water can, of course, be used for human consumption, after extensive treatment, but the cost factor becomes prohibitive and the community is compelled to look for some other sources of supply. The property on the banks of such a stream, may also lose its value, due to the odors from the stream and its unhealthy look.

In nature, clean waters are generally saturated with the dissolved oxygen or nearly so (2), clear and healthy to look at and without any odors. When domestic or industrial wastewaters are discharged into such water, a succession of changes in water quality takes place. The initial effect of the pollution is to degrade the physical quality of water, by the presence of dissolved or suspended pollutants. Gradually, as the pollutants are utilized as food, and oxidised to gain energy for sustaining aquatic life, a shift to biochemical degradation takes place, and a lot of new organic compounds, some toxic to certain forms of aquatic life, are produced as a result of decomposition of the organic matter. In the biochemichal oxidation of the pollutants, the oxygen required is derived from the dissolved oxygen content of the stream. This causes a depletion in the D.O. content of the water. As soon as the D.O. falls below the saturation level, the atmospheric oxygen dissolves in water to make up for the loss. The surface layer becomes saturated almost instantaneously and therefore the rate of dissolution of the atmospheric oxygen in water, called reaeration, depends upon the

turbulence present in it, which determins the amount of mixing or renewal of the top layer in the stream. Both the rate of deoxygenation of water due to the biochemical degradation and the rate of reaerntion determine the amount of D.O. present in a stretch of polluted stream at any moment. Thus we can picture the dissolved oxygen as an asset (or credit) and the biochemical oxygen demand of the pollutants present as the liability (or debit) of the stream. By measuring the D.O. content of a stream, one can fairly judge, as to what extent is the stream polluted and whether its water can be economically put to the various beneficial uses.

Thus, the maintenance of a minimum D.O. content provides us with a controlling criteria for the discharge of domestic and industrial wastewater in a stream. For optimisation of wastewater treatment facilities and the optimum utilization of the capacity of the stream to assimilate pollution, without any harmful effects, it is necessary to predict with a fair accuracy, the D.O. concentration downstream of a wastewater outfall. This prediction has for long been based principally on the classical first order biochemical degradation reaction kinetics theory forwarded by Streeter and Phelps (3,4). The Streeter Phelps equation is based on the assumption that there are only two major processes taking place, which are: (a) comsumption of oxygen in the satisfaction of B.O.D. along the stretch by the biochemical oxidation of the organic matter; and (b) replacement of oxygen by reaeration at the surface. Recently it has been pointed

out by many research workers, that the processes other than the two assumed to be present by Streeter and Phelps are also taking place simultaneously and must be accounted for while assesing the quality of water in a stream. Some of these processes are :(5):

(i) B.O.D. removal by sedimentation and/or adsorption.

(ii) B.O.D. addition by bottom deposit scour, and diffusion of partly decomposed products of benthal decomposition.

(iii) Addition of B.O.D. along the stretch by local runoff.

(iv) Removal of oxygen from water to aerobic zone of benthal decomposition.

(v) Removal of oxygen from water by purging action of gasses rising from the benthal layer.

(vi) Oxygen addition by photosynthesis in plankton.

(vii) Oxygen removal by respiration of plankton and fixed plants.

(viii) Continuous redistribution of both the B.O.D. and oxygen by the effect of longitudinal mixing.

The generally accepted model for predicting dissolved oxygen concentration in a polluted stream, given by equation 2.1.3, developed by HW Streeter and EB Phelps (3,6,7), is based on the first order reaction kinetics for both, the exertion of biochemical demand (8,9,10) and for reaeration (6). The use of a first order reaction kinetics for the exertion of B.O.D. has been questioned by a number of investigators, and alternative

higher order reaction kinetics have been proposed (11,12,13,14). The process of biochemical oxidation of organic matter involves: (a) conversion of the substrate into biomass with varying degree of synthesis and (b) utilization of stored decomposition products and of cell structure. The later phase involves both the oxidative micro-organisms and their predators. This clearly reflects on the relative importance of the concentration of micro-organisms too. Its importance can be better estimated by imagining the substrate available as the raw material in a factory and the micro-organisms as the workers, to convert the raw material into the finished products, carbon-di-oxide and water in the case of the stream.

Let us imagine a sterile medium containing some bio-degradable matter, and enough D.O. to sustain aerobic life, had it been there. Since there are no micro-organisms or biochemical agencies present, to oxidise the substrate, no B.O.D. will be exerted and there would be no change in its D.O. content. Now, suppose, in two identical and equal portions of this medium, we introduce micro-organisms capable of degrading this substrate, one organism in one portion and two in the other. Naturally the substrate should be expected to be consumed and in the process, B.O.D. exerted, in the second sample at a rate, twice of that in the first one. Projecting the same to the normal concentrations of micro-organisms, present in natural waters, the importance of consideration of the concentration of micro-organisms can be appreciated. It becomes even more obvious when one bears in mind that one of the factors affecting

The D.O. in a water body is the exertion of B.O.D.; and for which we should have a substrate to be degraded and the micr-oorganisms to do it.

A second order model, involving both, the concentrati-ons of substrate and that of the micro-organisms, is proposed and investigated in this study. It takes into consideration the microbial concentration, according to the Monod's expression for consumption of organic matter, based upon Mechaelis-Menton hypothesis. Monod's work (15) on microbial growths in Chemostats has contributed significantly towards a deeper understanding of the principles involved, and the role of the concentration of the micro-organisms in the exertion of B.O.D. Recent experiments on the study of concentration effects in the biological oxidation of trade wastes by Wilson (16) have extended Monod's results obtained for pure cultures, to heterogenous mixed cultures, thus making them applicable to Sanitary Engineering problems.

The term representing the dissolved oxygen consumed in the biochemical oxidation of the substrate is derived from the Monod's expression, which involves the concentration of both; the substrate and the micro-organisms. Thus the effect of the microbial population on the dissolved oxygen is accounted for. As the biochemical degradation of even simple compounds like glucose consists of many intermediate steps, involving numerous intermediate products, with their own rate of reaction the slowest of which becomes the governing criteria for the overall rate of reaction. But to determine the exact rate of reaction, one will first have to identify this slowest step and measure the concentrations of various enzymes involved, reactants and

intermediate products at that stage. Now, this may not always be an easy job, specially in the light of the fact that the whole chain of reactions, the slowest step and the involved chemical and biochemical agencies will be different for the different pairs of substrate and micro-organisms. These complications will further be increased in the case of mixed cultures of micro-organisms, involving various types and species of organisms. The situation will become even more complex for the complex substrates like proteins and other natural products. If we make a reasonable assumption, that the microbial concentration represents the overall biochemical activity, which is justified, because afterall, all the enzymes and other necessary biochemical agencies have to come from the micro-organisms themselves, then we can safely say that the rate of reaction will depend upon the concentration of substrate and the micro-organisms present at any instant and hence, the reaction will be a second order one.

1.2 AIM AND SCOPE OF THE STUDY

The main aim of the author in taking up this study has been to investigate into the effect of both the microbial population and the substrate concentration on the dissolved oxygen content of a polluted stream. A comparison of this rational model with the Streeter - Phelps equation is also to be made, with the primary aim of bringing out the inadequacy of the later formulation in dealing with the practical situations.

This study has been limited mainly to the following

horizons:

1. To formulate a rational model for dissolved oxygen profile in a stream, giving,the microbial concentration its due recognition.
2. To verify the model experimentally on a simulated model of a plug flow type stream.

The numerical solutions of the mathematical formulations are worked out on the IBM 7044 digital computer . A few, model dissolved oxygen profiles for varying initial conditions are plotted experimentally and compared with the theoretical solutions of the proposed model for verification.

CHAPTER II

LITERATURE REVIEW

2.1 FIRST ORDER KINETICS FOR B.O.D. REACTION & EQUATION FOR D.O. PROFILE BASED ON THAT:

The classical, first order theory for the reaction kinetics of the exertion of B.O.D., developed by Streeter and Phelps (3,4) states: "The rate of the biochemical oxidation of organic matter is proportional to the remaining concentration of unoxidised substances, measured in terms of oxidizability" (4). This law, expressed in the differential form becomes:

$$-\frac{dL}{dt} \propto L$$

$$\text{or} \quad -\frac{dL}{dt} = k_1 L$$

where, L = B.O.D. present at any instant t .

k_1 = Constant of proportionality, the B.O.D. reaction rate constant

Integrating from, $t = 0$, $L = L_a$ to $t = t$, $L = L$, we get

$$L = L_a e^{-k_1 t} \qquad \ldots\ldots \quad 2.1.1$$

The expression representing the dissolved oxygen profile (or sag curve), based on this theory, developed by H.W. Streeter (6,3) and analysed by G.M. Fair (7) is given by

$$\frac{dD}{dt} = k_1 L - k_2 D \qquad \ldots\ldots \quad 2.1.2$$

which upon integration yields,

$$D = \frac{k_1 L_a}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) + D_a e^{-k_2 t} \qquad \ldots \quad 2.1.3$$

where, D = Oxygen deficit, at a point distant, time of flow t,

D_a = Oxygen deficit at the reference point, at t = o

L_a = Ultimate first stage B.O.D. at the reference point, at t = o

k_2 = reaeration rate constant

2.2 EFFECT OF SCOURING, DEPOSITION, PHOTOSYNTHESIS, AND BENTHAL DECOMPOSITION:

H.A. Thomas, Jr., (21) in 1948, pointed out that, deposition and scouring of the suspended matter and stream bed sediment respectively, must also be taken into account, and included another constant k_3, in equation 2.1.3 above. He postulated that the rate of deposition and scouring is proportional to the remaining B.O.D. and modified equation 2.1.3 to the form:

$$D = \frac{k_1 L_a}{k_2-(k_1+k_3)} \left(e^{-(k_1+k_3)t} - e^{-k_2 t}\right) + D_a e^{-k_2 t} \quad . . \quad 2.2.1$$

where, k_3 = the constant of proportionality, reflecting the composition of waste and the receiving water (regarding the suspended matter), and the quiesence of the stream at the point under consideration.

The negative value of k_3, indicated scour, reversing the process of deposition.

Dobbins (5) brought up the importance of addition of B.O.D. from benthal layer and local runoff; removal of oxygen by benthal demand and plant respiration; and addition

of oxygen by photosynthesis. He made the following assumptions:

1. The Stream flow is steady and uniform.
2. The process for the stretch as a whole is a steady state process, the conditions at every cross section being unchanged with time.
3. The removal of B.O.D. by both the bacterial oxidation and the sedimentation or adsorption or both, are first order reactions, the rates of removal at any section being proportional to the amount present.
4. The removal of oxygen by benthal demand and by plant respiration, the addition of oxygen by photosynthesis and the addition of B.O.D. from the benthal layer or the local runoff are all uniform along the stretch.
5. The B.O.D. and oxygen are uniformly distributed over each cross section, thus permitting the equation to be written in the usual one dimensional form.

Based on the above assumptions Dobbins proposed the following expression for the prediction of B.O.D. remaining and oxygen deficit down stream a pollution point:

$$D = \frac{k_1 \left(L_A - \frac{L_a}{k_1+k_3}\right)\left(e^{-(k_1+k_3)t} - e^{-k_2 t}\right)}{k_2 - (k_1+k_3)} + D_o\, e^{-k_2 t}$$

$$+ \left(\frac{D_B}{k_2} + \frac{k_1 L_a}{k_2(k_1+k_3)}\right)\left(1-e^{-k_2 t}\right) \quad \ldots\ldots 2.2.2.1$$

$$L = L_A\, e^{-(k_1+k_3)t} + \frac{L_a}{k_1+k_3}\,(1-e^{-(k_1+k_3)\,t}) \quad \ldots \quad 2.2.2.2$$

where, L = B.O.D. remaining at a time t

L_A= Initial B.O.D.

L_a= rate of addition of B.O.D. along the stretch

D = Dissolved oxygen saturation Deficit

D_o= Initial Dissolved Oxygen Saturation Deficit

D_B= Rate of removal of D.O. along the stretch by benthal demand and the effect of plants

k_1= Rate of constant for trological oxidation

k_2= Reaeration constant

k_3= rate constant for B.O.D. removal bysedimentation or adsorption.

Another equation for the D.O. profile between the stations a and b proposed by Camp (22) in 1965, includes and accentuates the photosynthetic reaeration of water due to algae and other aquatic plants, as compared to the atmospheric reaeration, is

$$D_b = \frac{k_1}{k_2-(k_1+k_3)}\left(L_a-\frac{p}{2.3(k_1+k_3)}\right)\left(10^{j_1 x}-10^{j_2 x}\right)$$

$$+\frac{k_1}{k_2}\left(\frac{p}{2.3(k_1+k_3)}-\frac{\alpha}{2.3\,k_1}\right)(1-10^{j_2 x})+D_a\,10^{j_2 x} \quad \ldots \quad 2.2.3$$

where, $j_1 = 0.434\left(\frac{U}{2\epsilon}-\frac{U^2}{4\epsilon^2}+\frac{2.3(k_1+k_3)}{\epsilon}\right)$ 2.2.3.1

$$j_2 = 0.434\left(\frac{U}{2\epsilon}-\frac{U^2}{4\epsilon^2}+\frac{2.3\,k_2}{\epsilon}\right) \quad \ldots \quad 2.2.3.2$$

D_a = Average oxygen saturation deficit, over the cross section at river station 'a', Steady state, in ppm

D_b = Average oxygen saturation deficit, over the cross section at river station 'b', steady state, in ppm

k_1 = deoxygenation constant, day^{-1}

k_2 = atmospheric reaeration constant, day^{-1}

k_3 = rate constant for settling out of B.O.D., day^{-1}

L_a = average steady state first stage oxygen demand at river station a, ppm

p = rate of addition of B.O.D. to overlying water from bottom deposites, ppm/day

α = rate of production of D.O. by algae through photosynthesis.

U = average velocity of river between stations a and b, miles/day

ϵ = longitudinal mixing coefficient between river stations 'a' and 'b', square miles/day

x = distance between stations 'a' and 'b', miles

O'Connel et.al. (23), proposed the following model for the D.O. profile, based upon the studies of the Truckee River in Nevada State, U.S.A., stressing upon the effect of benthic algae on the stream D.O.

$$D_t = \frac{k_1 L}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right) - \frac{P-R}{k_2} \left(1 - e^{-k_2 t}\right) + D_a \, e^{-k_2 t} \quad \ldots \; 2.2.4$$

where, P-R = net oxygen contribution by photosynthetic activity

P = oxygen gain by photosynthesis

R = oxygen consumed in algal respiration

D_t = dissolved oxygen saturation level deficit

D_a = Initial dissolved oxygan saturation level deficit

k_1 = deoxygenation constant

and, k_2 = reaeration constant

Akerlindh (24) emphasised the importance of the importance of the immediate oxygen demand and the oxygen demand exerted by the bottom sludge, and proposed the following equation for the D.O. profile

$$D = \frac{k_i L_i}{k_r - k_i}\left(e^{-k_i t} - e^{-k_r t}\right) + \frac{k_b L_b}{k_r - k_b}\left(e^{-k_b t} - e^{-k_r t}\right) + \frac{k_s L_s}{k_r - k_s}\left(e^{-k_s t} - e^{-k_r t}\right) + D_a\, e^{-k_r t} \quad \ldots\ldots \quad 2.2.5$$

where, D_a = Initial dissolved oxygen saturation deficit, ppm

L_i = Initial immediate oxygen demand, ppm

L_b = Initial B.O.D. in the stream, due to "flowing pollutional load", i.e. dissolved matter and non-depositing suspended matter, ppm

L_s = B.O.D. in the stream due to "depositing pollutional load", ppm

k_i = specific rate coefficient of deoxygenation due to L_i

k_b = specific rate coefficient of deoxygenation due to L_b

k_s = specific rate coefficient of deoxygenation due to L_s

k_r = specific rate coefficient of reaeration

t = time of flow in days.

2.3 SECOND OR HIGHER ORDER EXPRESSIONS FOR B.O.D. REACTION KINETICS:

Many research - workers have questioned Streeter - Phelps first order B.O.D. reaction theory, in order to arrive at a better coordination of theoretical and experimental data of exertion of B.O.D. and prediction of D.O. profile. Several alternative expressions have been proposed, some of which are alternative expression for the exertion of B.O.D. as

$$y_t = S(M \log t + B) \quad \ldots\ldots\ldots\ldots \quad 2.3.1$$

where, y_t = ultimate B.O.D. at the end of the stage

S = 5-day B.O.D. intercept of the line

$M = \frac{m}{s}$ = B.O.D. rate parameter

$B = \frac{b}{s}$ = B.O.D. rate parameter

m = slope of the plot of y_t v/s log t (straight line)

b = intercept of the plot of y_t v/s log t

The values of M and B were found to be 0.85 and 0.41 respectively for the domestic sewage.

Suggesting that the rate of removal of sustrate is proportional to the square of the remaining substrate, Young (13) proposed the following second order differential equation for the exertion of B.O.D.:

$$\frac{d}{dt}(L - y) = k(L - y)^2 \quad \ldots\ldots 2.3.2$$

Integrating, we get

$$y = \frac{t}{\frac{1}{kL^2} + \frac{1}{L}t} \quad \ldots\ldots 2.3.3$$

where, L = initial substrate concentration (at t = 0)

t = time

y = B.O.D. satisfied by time t

ReVelle et.al. (14) emphasised on the importance of:

(i) The rate of removal of the substrate is proportional to the product of the concentration of substrate and bacteria.

(ii) The bacterial population is proportional to the amount of food removed.

On the basis of these assumptions, they proposed the following expression for the exertion of B.O.D.

$$y = L - \frac{b + L}{\frac{b}{L}e^{k(L+b)t_{+1}}} \quad \ldots\ldots 2.3.4$$

where, y = B.O.D. expressed at time t (days); mg/l.

L = Ultimate B.O.D., mg/l

b = a constant representative of initial bacterial population, mg/l

k = rate constant ($(mg/l)\,day)^{-1}$

2.4 SECOND ORDER D.O. PROFILE EQUATIONS:

Dresnack et.al. (32) proposed the following two second order partial differential equations for B.O.D. and D.O. along a stretch of polluted natural stream, analogus to the equation representing the conduction of heat in solids:

$$\frac{\partial L}{\partial t} = D_L \frac{\partial^2 L}{\partial x^2} - U\frac{\partial L}{\partial x} - (k_1+k_3)\, L+L_a \quad . \quad . \quad . \quad 2.4.1.1$$

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x} - U\frac{\partial C}{\partial x} - k_1 L + k_2 (C_s-C) - D_B \quad . \quad . \quad 2.4.1.2$$

where, L = first stage B.O.D., ppm

C = dissolved oxygen concentration, ppm

C_s = Saturation dissolved oxygen concentration, ppm

D_L = coefficient of longitudinal dispersion, sqmiles/day

U = average stream velocity, miles/day

k_1 = B.O.D. reaction rate constant, day^{-1}

k_2 = reaeration rate constant, day^{-1}

k_3 = rate of removal of B.O.D. by sedimentation and adsorption or both, day^{-1}

L_a = rate of addition of B.O.D. along the stretch

D_B = Net rate of removal of D.O. by all processes other than biochemical oxidation of the flowing B.O.D. load, ppm/day

x = distance along the stretch, miles

t = time, days

Equations 14 and 15, solved by finite difference method, yield

$$L_{i,n+1}\left(1+\frac{k(k_1+k_3)}{2}\right) = L_{i-1,n}\left(\frac{k D_L}{h^2}\right) + L_{i,n}\left(1-\frac{k(k_1+k_3)}{2}-\frac{2kD_L}{h^2}\right)$$

$$+ L_{i-1,n}\left(\frac{kD_L}{h^2}\right) + k L_a \quad \ldots \quad 2.4.1.3$$

and

$$C_{i,n+1}\left(1+\frac{k\,k_2}{2}\right) = C_{i-1,n}\left(\frac{k D_L}{h^2}\right) + C_{i,n}\left(1-\frac{k\,k_2}{2}-\frac{2kD_L}{h^2}\right)$$

$$+C_{i+1,n}\left(\frac{kD_L}{h^2}\right) + k\,k_2\,C_s - k\,D_B - (L_{i,n}+L_{i,n+1})\frac{kk_1}{2} \quad \ldots 2.4.1.4$$

where, k = time mesh interval

2.5 OTHER EXPRESSIONS FOR D.O. PROFILE:

Many workers have avoided the usual deoxygenation - reoxygenation approach in giving suitable expressions for the dissolved oxygen profiles and gave some emperical formulae or some expressions based on some other kinds of theory. An expression proposed by Churchill and Buckingham (25), thus completely avoids the use of the usual deoxygenation and reoxygenation coefficients, k_1 and k_L, by making a statisfical fit of observed data according to the assumed relations:

$$\text{D.O. drop} = a + b\,L(5) + c\,T + d/Q \quad \ldots \quad 2.5.1$$

where D.O. drop = difference in ppm, between the D.O. at a location above the single pollution source and the D.O. level at the critical point of the sag curve.

L(5) = Five day B.O.D. in ppm, measured at a location in the vicinity of the critical point.

T = Water temperature, ^oC

Q = Stream flow, cfs

a,b,c,d = constants to be determined by statistical analysis of data obtained from a set of observed D.O. profiles.

For a stream with a discharge that is steady at any particular cross section, but which may vary along the course due to the distributed surface runoff and groundwater, Wen-Hsiung Li (26) gave the following expression:

$$C_s - C = e^{-\phi_2}\left[C_s - F(\xi) + \int_0^x \frac{1}{V} k_a (C_s - C_a)\, e^{\phi_2} dx \right.$$

$$\left. + f(\xi) \int_0^x \frac{1}{V} k_1\, e^{\phi_o} dx + \int_0^x \frac{1}{V} k_1 I\, e^{\phi_o} dx \right] \quad \ldots \quad 2.5.2$$

where, C_s = D.O. at saturation

$C(x,t)$ = D.O. in mass per unit volume of water

$C_a(x)$ = D.O. of added discharge

$F(t)$ = D.O. of stream water at out fall i.e. $C(0,t)$

$f(t)$ = B.O.D. at cross section of out fall after mixing with stream.

$\xi = t - \int_0^x \frac{dx}{V} = t - T$

t = time

x = distance along the stream

$V(x)$ = speed of flow = Q/A

$A(x)$ = Cross sectional area of stream

$K_a(x)$ = Dilution coefficient $\frac{1}{A}\frac{dQ}{dx}$

$k_1(x)$ = Coefficient of oxygen consumption (monomolecular formula)

$k_2(x)$ = Coefficient of reaeration

$I(x) = \frac{K_a L_a}{V} e^{\phi_1} dx$

$$\phi_1(x) = \frac{k_1+k_a}{V}\,dx$$

$$\phi_2(x) = \frac{k_2+k_a}{V}\,dx$$

$$\phi_o(x) = \frac{k_2-k_1}{V}\,dx = \phi_2(x)-\phi_1(x)$$

This model assums that the D.O. and B.O.D. of added surcharge along the stream, downstream to the outfall concerned is steady at each point, but not necessarily uniform along the course of the stream. The D.O. and B.O.D. at the outfall may fluctuate with time. Well mixed conditions, both vertically and laterally have been assumed, so that the problem is essentially one dimensional.

Thoman (27) has proposed the following mathematical model based on the concepts of "systems analysis" for the D.O. in streams

$$C(t) = C_{os}\,A(w)\,\cos(\omega t + \theta + \alpha(w)) \quad \ldots \quad 2.5.3.1$$

This is a linear system, much oversimplified and is rarely met in nature. Thoman goes ahead to generalise this model to the form

$$C_j(t) = \bar{d}\sum_{i=1}^{n} J_{ok}\left[A_{ki}(w)\right]_{JL}\left[A_{ij}(w)\right]_{LC}\cos\left[Wt+\left\{\theta_{ki}(w)\right\}_{JL} + \left\{\theta_{ij}(w)\right\}_{LC}\right] \quad \ldots \quad 2.5.3.2$$

where, $C_j(t)$ = D.O. in mg/l

$C_{si}(t)$ = Saturation D.O. varying in a periodic form with the temperature of water, over the year

C_{os} = amplitude of $C_{si}(t)$

ω = angular frequency of $C_{si}(t)$

$\theta_{ij}(w)$ = phase angle shift of $C_{si}(t)$

$A_{ij}(w)$ = Amplitude attenuation of $f_i(t)$ for solution of $C_j(t)$

$d_i(t)$ = Decay coefficient in system i

$J_i(t)$ = treatment plant forcing function in system i

A simple emperical equation of calculation of D.O. drop downstream to a pollution, was given by Smith et.al (28) as follows:

$$Y = \frac{K\ B\ 2^{T/10}}{F} \quad \ldots\ldots\ldots\ 2.5.4$$

where, Y = D.O. drop in ppm

B = B.O.D. loading in thousands of lbs/day

F = Stream flow in mg/d

T = Temperature of stream in ^{o}C

K = proportionality factor

Okun et.al (29) studied the waters of Catawba river in south Carolina, U.S.A. and fitted the 188 days recorded, to a general equation given below, and obtained a multiple correlation coefficient of 0.970.

$$Y = 9.47-0.49\ x_1-0.07\ x_1x_1+0.019\ x_1x_2+0.00096\ x_1x_3 -7.1\ x_1x_4-0.341\ x_2-0.00035\ x_2x_2+0.00528\ x_2x_3+4.3x_2x_4 -0.0839\ x_3+0.00017\ x_3x_3-2.0\ x_3x_3-2.0\ x_3x_4+30\ x_4 +840\ x_4x_4 \quad \ldots\ldots\ 2.5.5.1$$

where, Y = D.O. in mg/l

x_1 = Intake D.O. mg/l

x_2 = River flow, 1000 cfs

x_3 = Temperature, ^{o}C

x_4 = Discharge ratio (Waste: River)

This equation being mathematically cumbersome, was further simplified by the authors, eliminating several terms which have little value for prediction purposes without any loss of accuracy, and its final form came to be

$$Y = 8.88 - 0.44\ x_1 + 0.068\ x_1x_1 + 0.012\ x_1x_2 - 0.19\ x_2 - 0.059\ x_3 - 32.7\ x_4 \quad \ldots\ 2.5.5.2$$

O'Connor (30) with the help of a set of linear differential equations, evolved the following equations for prediction of oxygen deficit in the streams:

$$D = \frac{K\ l_d}{k_2 - k}\left[\left\{e^{\pm jx}\,\mathrm{Sinh}(jd)\right\} - \left\{\frac{k}{k_2}e^{\pm j_2 x}\,\mathrm{Sinh}\ (j_2 d)\right\}\right] \quad \ldots\ 2.5.6.1$$

for $-\infty \leq x \leq -d$ and $+d \leq x \leq +\infty$

and

$$D = \frac{k\ l_d}{k_2 - k}\left[\left\{1 - e^{-jd}\cosh\ (jx)\right\} - \frac{k}{k_2}\left\{1 - e^{-jd}\mathrm{Cosh}(jx)\right\}\right] \quad \ldots\ 2.5.6.2$$

for $-d \leq x \leq +d$

where, D = oxygen deficit

l = B.O.D. concentration = $l_a\ e^{\pm jx}$

$$l_a = \frac{W}{2A\sqrt{KE}}$$

$$l_d = \frac{W}{A\sqrt{K}}$$

j = K/E = flux

W = daily mass rate of discharge of B.O.D.

A = Cross sectional area

E = dispersion coefficient

k_2 = reaeration coefficient

x = distance along the stream

Uniform load is assumed to be from - d to + d.

CHAPTER III

THEORETICAL BACKGROUND

The model investigated in this study is based on Monod's expression describing the kinetics of becoxidation of organic matter as described below.

Defining μ as the rate of growth of microorganisms in lograthmic phase, or

$$\mu = \frac{d}{dt} \ln(x)$$

where, x = concentration of microorganisms

μ = growth rate constant

we have,

$$\mu = \frac{1}{x} \frac{dx}{dt}$$

$$\text{or, } \frac{dx}{dt} = \mu x \qquad \ldots\ldots\ldots \quad 3.1$$

Monod (15) showed, that, for pure cultures, which was later extended by Wilson (16) to mixed cultures, applicable to sanitary engineering systems,

$$\mu = \frac{\mu_{max} S}{K_s + S} \qquad \ldots\ldots\ldots \quad 3.2$$

where, μ_{max} = maximum value of growth rate constant (μ) with unlimitted substrate.

K_s = Michaelis - Menton constant, given by substrate concentration at which the observed growth rate is one half of its maximum value (i.e. $= \frac{1}{2} \mu_{max}$).

S = concentration of substrate at the instant t

Combining the equations 3.1 and 3.2, we get

$$\frac{dx}{dt} = \frac{\mu_{max}\, S}{K_S + S}\, x \qquad \ldots\ldots\ldots 3.3$$

Also since,

$$x = x_o + \frac{1}{K_x}(S_o - S) \qquad \ldots\ldots\ldots 3.4$$

where, x_o = initial concentration of microorganisms

S_o = initial concentration of substrate

K_x = substrate consumed per unit mass of microorganisms synthesised, or reciprocal of "yield coefficient $Y_{x/s}$".

Expressing in a differential form equation 3.4 becomes

$$-\frac{ds}{dt} = K_x \frac{dx}{dt} \qquad \ldots\ldots\ldots 3.5$$

Substituting the value of dx/dt from equation 3.3, and the value of x from equation 3.4, we get

$$\frac{ds}{dt} = -\mu_{max} \frac{S(A-S)}{K_s + S} \qquad \ldots\ldots\ldots 3.6$$

where, $A = K_x x_o + S_o$

Integrating* equation 3.6, we get

$$t = \frac{1}{\mu_{max}} \ln \left[\left(\frac{A-S}{A-S_o} \frac{S_o}{S} \right)^{K_S/A} \cdot \frac{A-S}{A-S_o} \right] \qquad \ldots\ldots 3.7$$

---

*Steps of integration shown in the appendix

3.1 THE DISSOLVED OXYGEN MODEL:

Writing a mass balance equation, for the dissolved oxygen, for an aerobic biochemical system, we have,

$$\begin{bmatrix}\text{Change in oxygen content of the system}\end{bmatrix} = \begin{bmatrix}\text{Change in the oxygen content due to substrate metabolism}\end{bmatrix} + \begin{bmatrix}\text{Change in the oxygen content due to endogeous metabolism}\end{bmatrix} + \begin{bmatrix}\text{Change in the oxygen content due to reaeration from atmosphere}\end{bmatrix}$$

or,
$$V\left(\frac{dC}{dt}\right)_{overall} = V\left(\frac{dC}{dt}\right)_{\substack{substrate\\metabolism}} + V\left(\frac{dC}{dt}\right)_{\substack{endogenous\\metabolism}} + V\left(\frac{dC}{dt}\right)_{reaeration}$$

or,
$$\frac{dC}{dt} = \frac{dC}{dS} \cdot \frac{dS}{dt} + \frac{dC}{dx} \cdot \frac{dx}{dt} + K_2 (C_s - C)$$

where, K_2 = reaeration rate constant, day^{-1}

C = dissolved oxygen concentration at time t, mg/l.

C_s = saturation dissolved oxygen concentration under the existing physical conditions, mg/l.

As under endogenous conditions (31).

$$\frac{dx}{dt} = -K_e\, x \qquad \ldots\ldots\ldots\ldots \quad 3.1.2$$

where, K_e = Endogenous death rate constant

Substituting the values of $\frac{d_s}{dt}$ from equation 3.6 and that of $\frac{dx}{dt}$ from equation 3.1.2 in equation 3.1.1, we get,

$$\frac{dC}{dt} = - \mu_{max} \frac{S(A-S)}{K_s+S} \cdot \frac{dC}{dS} - K_e \times \frac{dC}{dx} + K_2 (C_s-C)$$

. . . . . 3.1.3

Now, substituting $C_s - C = D$, the dissolved oxygen deficit we get,

$$- \frac{dD}{dt} = - \mu_{max} \frac{S(A-S)}{K_s+ S} \cdot \frac{dC}{dS} - K_e \times \frac{dC}{dx} + K_2 D$$

$$\text{or,} \quad \frac{dD}{dt} + K_2 D = \mu_{max} \frac{S(A-S)}{K_s+ S} \frac{dC}{dS} + K_e \times \frac{dC}{dx}$$

$$\text{or,} \quad \frac{dD}{dt} + K_2 D = \mu_{max} \frac{S(A-S)}{K_s+ S} K' + K_e \left\{x_o + \frac{1}{K_x}(S_o-S)\right\} \frac{dC}{dx}$$

$$\text{or,} \quad \frac{dD}{dt} + K_2 D = \mu_{max} K' \frac{S(A-S)}{K_s+ S} + \frac{K_e K''}{K_x} (A-S)$$

. . . . . 3.1.4

where, $K' = \frac{dC}{dS}$ = ultimate oxygen demand per unit mass of substrate.

$K'' = \frac{dC}{dx}$ = ultimate oxygen demand per unit mass of microorganisms under endogenous conditions.

The above equation can also be written as

$$\frac{dD}{dS} \cdot \frac{dS}{dS/dt} + K_2 D = \left\{ \mu_{max} K' \frac{S}{K_s+S} + \frac{K_e K''}{K_x} \right\} (A-S)$$

$$\text{or,} \quad \frac{dD}{dS} + \frac{K_2}{dS/dt} D = \left\{ \mu_{max} K' \frac{S}{K_s+S} + \frac{K_e K''}{K_x} \right\} \frac{A-S}{dS/dt}$$

Substituting the value of $\frac{dS}{dt}$ from equation 3.6

$$\frac{dD}{dS} - \frac{K_2}{\mu_{max}\frac{S(A-S)}{K_S+S}} D = \left\{ \mu_{max} K' \frac{S}{K_S+S} + \frac{K_e K''}{K_x} \right\} \frac{A-S}{-\mu_{max}\frac{S(A-S)}{K_S+S}}$$

or, $$\frac{dD}{dS} = \frac{K_2}{\mu_{max}} \cdot \frac{K_S+S}{S(A-S)} D - \left\{ K' + \frac{K_e K''}{K_x \mu_{max}} \right\} \frac{K_S+S}{S} \quad \ldots\ldots 3.1.5$$

This equation has been solved numerically, as the analytical solution becomes quite complicated and cumbersome for the purpose of obtaining the data . It was solved numerically by Runge-kutta fourth order method on IBM 7044/1401 digital computer system using Fortain IV language.

3.2 DETERMINATION OF THE CONSTANTS

3.2.1 μ_{max}, K_S and K_X

Equation 3.3 upon integration yields (30),

$$\ln x = \mu_{max} t - \frac{K_S}{A} \ln \left\{ \frac{x}{A-K_X x} \frac{S_o}{x_o} \right\} \quad \ldots\ldots 3.2.1.1$$

where, $A = K_X x_o + S_o$

Rearranging this equation, we get,

$$\frac{1}{t} \ln \left(\frac{x}{x_o}\right) = \frac{\mu_{max}}{1+K_S/A} - \frac{K_S/A}{1+K_S/A} \cdot \frac{1}{t} \cdot \ln \frac{S_o}{A-K_X} \quad \ldots\ldots 3.2.1.2$$

Now substituting,

$$b = K_X/S_o \quad \ldots\ldots 3.2.1.2\ a$$

$$h = x - x_o \quad \ldots\ldots 3.2.1.2\ b$$

$$m = \mu_{max}/(1+K_S/A) \quad \ldots\ldots 3.2.1.2\ c$$

$$n = \frac{K_s/A}{1+K_s/A} \qquad \ldots\ldots\ldots \quad 3.2.1.2\ d$$

equation 3.2.1.2 becomes

$$\frac{1}{t} \ln (x/x_o) = n \frac{1}{t} \ln (1-bh) + m \quad \ldots\ldots 3.2.1.2\ e$$

This equation is linear in $\frac{1}{t} \ln (x/x_o)$ and $\frac{1}{t} \ln (1-bh)$ and will plot as a straight line for there two variable groups. The value of b can not be determined by direct measurement, and has to be fixed by a trial and error procedure. For this $\frac{1}{t} \ln (x/x_o)$ and $\frac{1}{t} \ln (1-bh)$ are plotted on an arithmatic graph paper (Fig. 1) for various values of b, till a straight line with a positive slope is obtained. Then using this value of b, the various constants are calculated from the following equations,

$$\mu_{max} = \frac{m}{1-n} \qquad \ldots\ldots\ldots\ldots \quad 3.2.1.2\ f$$

$$K_s = \frac{n}{1-n} A \qquad \ldots\ldots\ldots\ldots \quad 3.2.1.2\ g$$

$$K_x = b S_o \qquad \ldots\ldots\ldots\ldots \quad 3.2.1.2\ h$$

3.2.2 <u>K', K_e and K"</u>

Since the second term of the equation 3.1.1, representing the oxygen consumed in endogeous metabolism is

$$\left(\frac{dC}{dt}\right)_{\substack{\text{endogeous} \\ \text{metabolism}}} = \frac{dC}{dx} \cdot \frac{dx}{dt}$$

$$= K_e K'' x \qquad \ldots\ldots \quad 3.2.2.1$$

Also because, $dC = \frac{dC}{dx} \cdot dx$ . . . . . .

$$= K''\ dx$$

we can conclude that $C = k'' x$

Therefore, substituting in equation 3.2.2.1 we get,

$$\frac{dC}{dt} = - K_e C \qquad \ldots\ldots\ldots \quad 3.2.2.2$$

which is a first order kinetics equation with reaction rate constant as K_e . Therefore the constant K_e can be determined by the Fujimoto's Method (17).

Since K" is defined as

$K'' = \frac{dC}{dx}$ = ultimate oxygen demand of the microbial mass under endogenous conditions.

Therefore K" will be given by the ultimate oxygen demand L_o, in the Fujimoto's Method.

3.2.3 B.O.D. REACTION RATE CONSTANT

According to equation 2.1.1, the first order expression for the kinetics for the B.O.D. reaction is

$$L = L_a \; e^{-k_1 t}$$

Taking lograthins

$$\ln (L/L_a) = - K_1 T \qquad \ldots\ldots \quad 3.2.3.1 \text{ a}$$

As L represents the B.O.D. remaining at any time t, which is representative of the remaining substrate concentration, Therefore replacing L by S and L_a by S_o be consistent with the terminology followed so far, we get

$$\ln (S/S_o) = - K_1 t \qquad \ldots\ldots\ldots \quad 3.2.3.1 \text{ b}$$

Thus a straight line will be obtained by plotting $\ln (S/S_o)$ against t whose slope will give K_1, the B.O.D. reaction rate constant.

3.2.4 REAERATION RATE CONSTANT, K_2

The rate of reaeration or rate of change in dissolved oxygen concentration or oxygen deficit, is proportional to the oxygen deficit existing at any time t (2). Expressed mathematically,

$$\frac{dD}{dt} = - K_2 D \quad \ldots\ldots\ldots \quad 3.2.4.1$$

Integrating between limits from; at $t = 0$, $D = D_o$ to at $t = t$, $D = D$ we get

$$\ln (D/D_o) = - K_2 t \quad \ldots\ldots \quad 3.2.4.2\ a.$$

or

$$D = D_o e^{-K_2 t} \quad \ldots\ldots \quad 3.2.4.2\ b$$

where, $D = C_s - C$ = D.O. deficit at any time t, mg/l

$D_o = C_s - C_o$ = D.O. deficit at time $t = 0$, mg/l

C_s = Saturation D.O. level under the given physical conditions, mg/l

C = D.O. concentration at time t, mg/l

C_o = initial D.O. concentration at time $t = 0$, mg/l

K_2 = constant of proportionality, the reaeration rate constant, day^{-1}.

The data of dissolved oxygen at regular intervals, in deoxygenated water, when plotted as $\ln \frac{D}{D_o}$ against t, will yield a straight line, whose slope will give K_2.

CHAPTER IV

MATERIALS AND METHODS

4.1 EXPERIMENTAL TECHNIQUES AND EQUIPMENT

4.1.1 LABORATORY SIMULATION OF STREAM

A plug flow type stream was simulated in the laboratory by taking the solution of substrate in aerated water with nutrients necessary for growth, in a 12" x 4" ø cylindrical jars. The system was inoculated with known amount of seed microorganisms and aerated with the help of flocculating paddle stirrers. From time to time the microbial concentration and the remaining substrate concentration was measured, as described in the following sections.

4.1.2 SOURCE OF SEED MICROORGANISMS

The microorganisms for seed were cultured in a chemostat reactor fed on a glucose solution of C.O.D. 400 mg/l along with the necessary nutrients. This solution was fed from a continuous, constant flow feeder bottle into the reaction vessel aerated with compressed air, and the overflow was collected in the collector bottle. This effluent was centrifuged at 5000 rpm for 10 minutes to seperate the microorganisms from the suspension media containing substrate. The supernatant was decanted and the microorganisms were washed four times with phosphate buffer, to remove all traces of substrate, that might be adsorbed on them. After washing, the seed was resuspended in phosphate buffer and stored in a refrigerator, till used.

4.1.3 DETERMINATION OF CONSTANTS

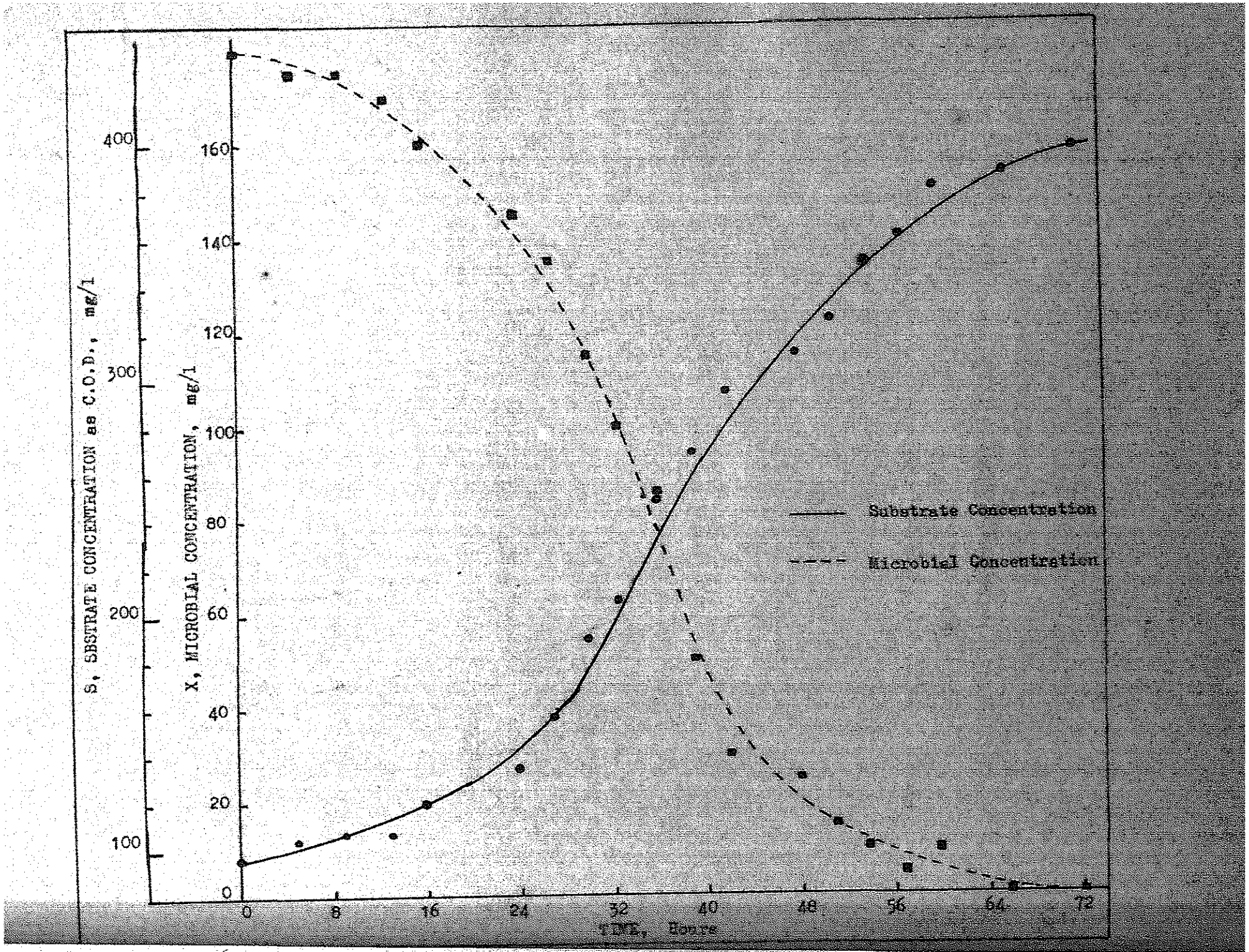
4.1.3.1 μ_{max}, K_s and K_x

A solution of substrate (glucose), C.O.D. 400 mg/l was taken with k_2HPO_4-KH_2PO_4 buffer and ammonium sulfate solution to provide phosphorus, control of pH and nitrogen for synthesis, was taken in 30 cm.x 10 cm. ø cylindrical jars, and inoculated with known amount of seed microorganisms, prepared as described above in the section 4.1.2. This was stirred by a flocculation paddle stirrer, to keep the whole thing mixed and aerated. The concentration of substrate as C.O.D. and that of the microorganisms was determined at regular intervals of time, as decribed below in section 4.2.1 and 4.2.2. This data was utilized to calculated the constants μ_{max}, K_s and K_x as described in sections 3.2.1 and 3.2.2 (Fig 1).

4.1.3.1 K', K_e and K"

The constants K', K" and K_e were determined with the help of Warburg Respirometer. The flask arrangement was kept as follows:

Substance	Flask 1 ml	Flask 2 (endogen- ml	Flask 3 (Thermobar-, ometer) ml
1. Main compartment,			
microbial suspension	1.5	1.5	1-
distilled water	-	1.0	2.5
2. Side Arm, glucose solution	1.0	-	-
3. Central Well, 6M KOH solution	0.1	0.1	0.1


S, SUBSTRATE CONCENTRATION as C.O.D., mg/l
X, MICROBIAL CONCENTRATION, mg/l
TIME, Hours
Substrate Concentration
Microbial Concentration
400
300
200
100
160
140
120
100
80
60
40
20
0
0
8
16
24
32
40
48
56
64
72

The respiration data obtained with flask 1 was used to determine K', the ultimate oxygen uptake per unit mass of the substrate (glucose), by Fujimoto's Method. The product K_e and K" was also determined by Fujimoto's Method, from the data obtained with flask 2 (Fig.2).

4.1.3.3 REAERATION RATE CONSTANT, K_2

Water was deoxygenated by adding sodium sulfite solution, 7.88 mg/l per mg/l of dissolved oxygen to be removed, under the catalytic of cobalt ion at a concertration 0.01 mg/l (18). This deoxygenated water taken in a 2.5 R, 30 cm. x 10 cm. ϕ cylindrical jar and aerated with the floculating stirrer at a known constant speed. The dissolved oxygen concentration was noted at regular intervals of time and K_2 was calculated according to the equation 3.2.4.2a (Fig.3).

4.1.4 THE SAG CURVES

A glucose solution of concentration of 25 mg/l was prepared in aerated water, and taken in five 30 cm x 10 cm ϕ cylindrical jars, to simulate a plug flow stream. These jars were inoculated with varying amounts of microbial suspension to obtain different S/X ratios. The initial microbial concentration was:

	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5
Microbial concentration mg/l.	2.1	4.2	6.3	8.4	10.5

The D.O. concentration was measured as described in section 4.2.3 for all these jars at the regular intervals of time. The contents of the jars were aerated by aerated by a flocculating stirrer at 70 rpm.

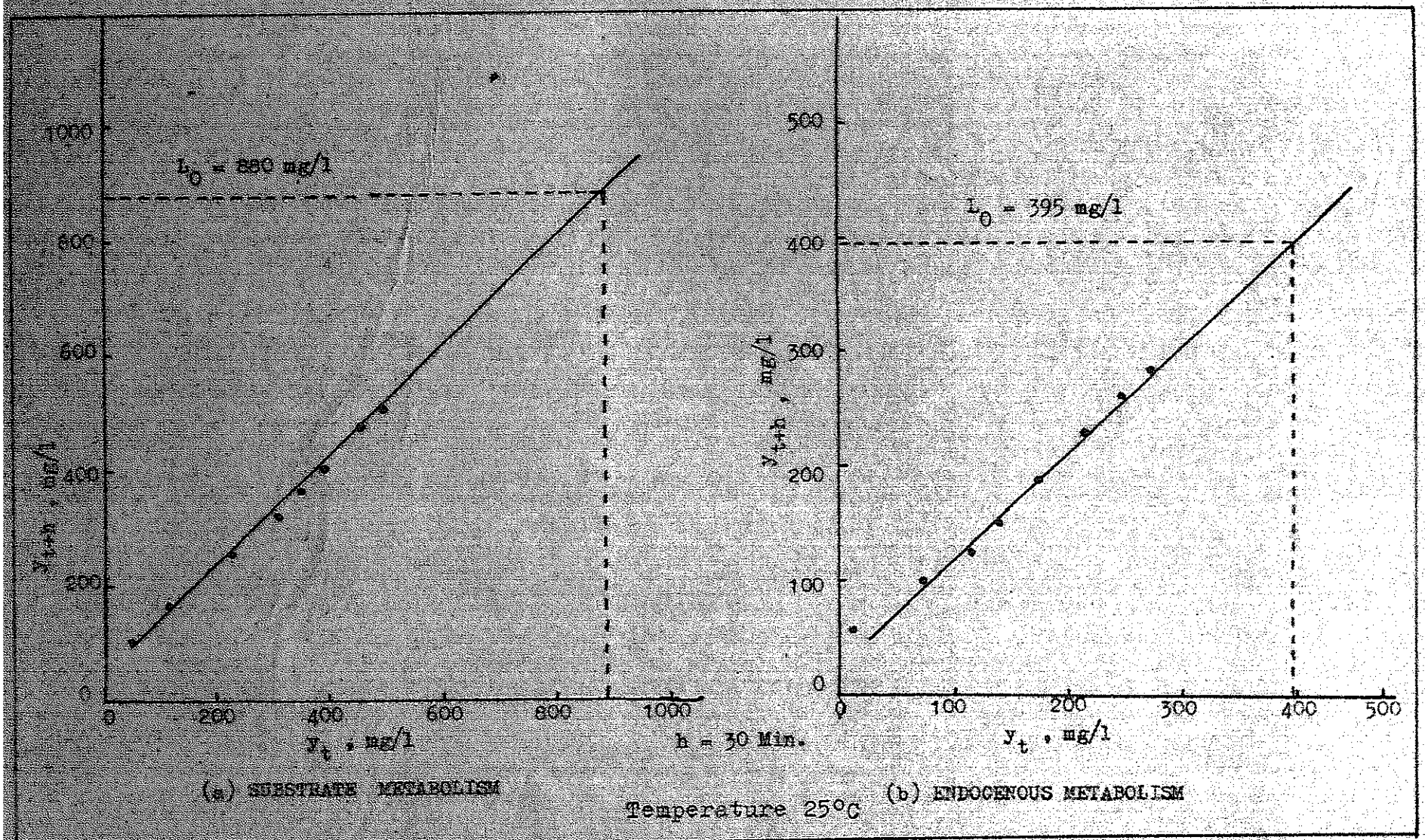


Figure 2 : CALCULATION OF k', k' AND K_e BY FUJIMOTO'S METHOD

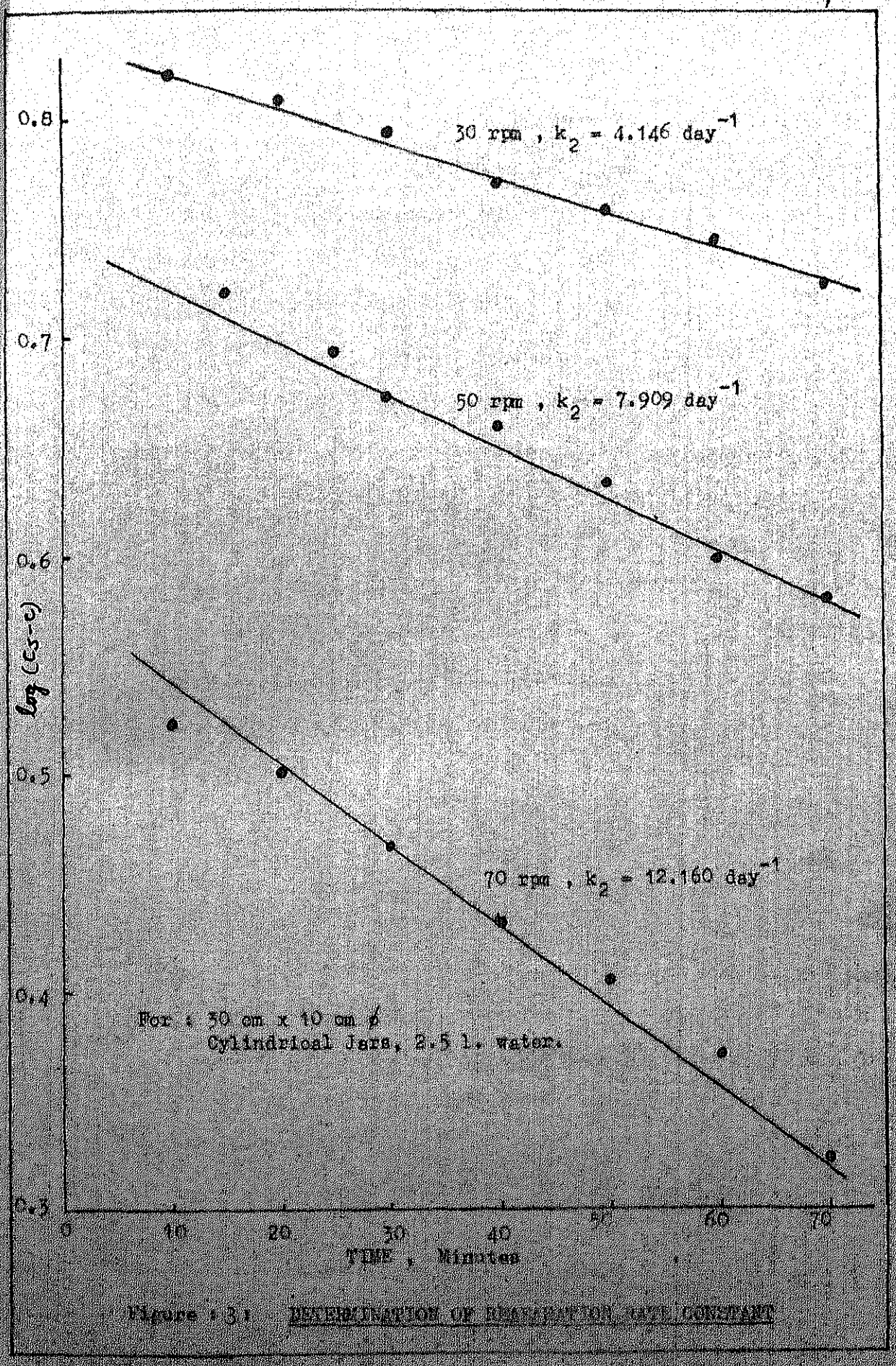


Figure : 3 : DETERMINATION OF REAERATION RATE CONSTANT

4.2 ANALYTICAL TECHNIQUES:

4.2.1 MICROBIAL CONCENTRATION

The gravimetric determination of microbial concentration for standardisation purposes was made by filtering a know volume of the microbial suspension under vacuum with the help of a filter pump, through a Whatman - 42 filter paper. The residue on the already weighed filter paper was dried at 120°C for two hours, cooled in a dessicator for 15 minutes and weighed again to determine the dry weight of biomass caught on the filter paper. The weight reading was taken after 5 minutes of taking the filter paper out of the dessicator, to standaridise the effect of moisture absorbed by the filter paper during the process of weighing. A calibration curve (Fig.4) of absorbance v/s microbial concentration as dry weight/l, determined gravimetrically as described above was prepared. The absorbance was meansured on a "spectronic - 20" spectrophotometer*, at 400 mμ wavelength. Later, during the experiments, the mixed liquor of the jars was pipetted out and its absorbance measured on the spectrophotometer. The corresponding concentration was then read off the calibration curve (Fig.4).

4.2.2 SUBSTRATE CONCENTRATION AS C.O.D.

To determine the C.O.D. of the jar liquor, to calculate the concentration of substrate remaining at any instant, the liquor was centrifuged at 5000 rpm for 10 minutes. The C.O.D. of clear supernatant was determined as per "Standard Methods of Examination of Water and Waste Water" (19).

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*Bausch & Lomb, U.S.A.

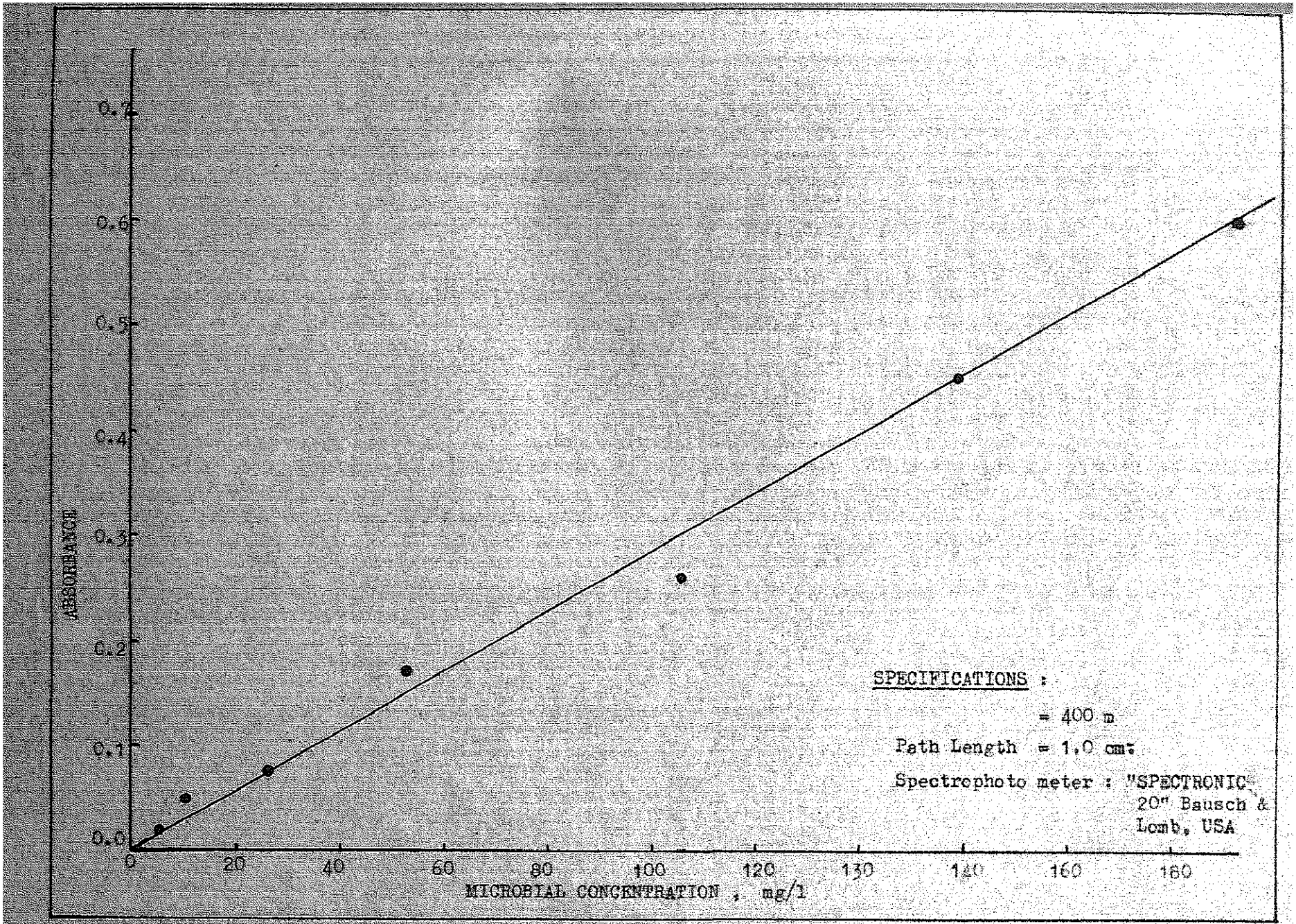

Figure 4 : CALIBRATION CURVE FOR MICROBIAL CONCENTRATION

4.2.3 DISSOLVED OXYGEN MEASUREMENTS

The dissolved oxygen concentration was measured by the help of a "Precision Galvanic Cell Oxygen Analyser"*. A calibration curve (Fig. 5) of the instrument reading v/s the actual dissolved oxygen concentration as determined by iodometric titration method (20) was prepared. Later, during the experiments the instrument reading was noted from time to time and the corresponding dissolved oxygen concentration read off the calibration curve.

---

*Precision Scientific Co., Chicago, U.S.A.

For : PRECISION GALVANIC OXYGEN ANALYSER
Precision Scientific Instruments Co., USA.
PROBE READING
0
1
2
3
4
5
6
7
8
9
10

CHAPTER V

RESULTS AND DISCUSSIONS

5.1 EVALUATION OF THE CONSTANTS

5.1.1 K_1, μ_{max}, K_s and K_x

From the data of the variation of substrate and the microbial concentration, obtained as described in section 4.2..3.1, ln (S/S_o) versus t is plotted in Figure No. 6 as a straight time. The B.O.D. reaction rate constant K_1, as described in section 3.2.3 is given by the slope of this line to be 0.04606 $hour^{-1}$. For calculating μ_{max}, K_s and K_x, $\frac{1}{t}$ ln (x/x_o) and $\frac{1}{t}$ ln (1-bh) are plotted on y and x axes respectively as described in section 3.2.1, for various values of b, till a straight line with a positive slope is obtained (Figure 7). This value of b comes out to be 0.006. Now μ_{max}, K_s and K_x are calculated by the equations 3.2.1.2 f, 3.2.1.2 g and 3.2.1.3 h and the following values are obtained,

$$\mu_{max} = 0.65 \text{ hr}^{-1} = 15.6 \text{ day}^{-1}$$

$$K_s = 415.0 \text{ mg/l}$$

$$K_x = 2.64$$

5.1.2 K', K" and K_e

The oxygen uptake data obtained with the Warburg respirometer, as described in section 4.2.3.1, is utilised to evaluate K', K" and K_e by Fujmoto's Method. In Figures 2 a, and 2 b, Y_{t+h} is plotted against Y_t, for the value of h as minutes. The ultimate oxygen uptake of the glucose solution of the concentration 1000 mg/l, turns out to be 880 mg/l, and therefore the value of K' or $\frac{dc}{ds}$, the ultimate oxygen consumption for glucose comes to be 0.88 mg/mg. mgO_2/mg glucose as C.O.D.

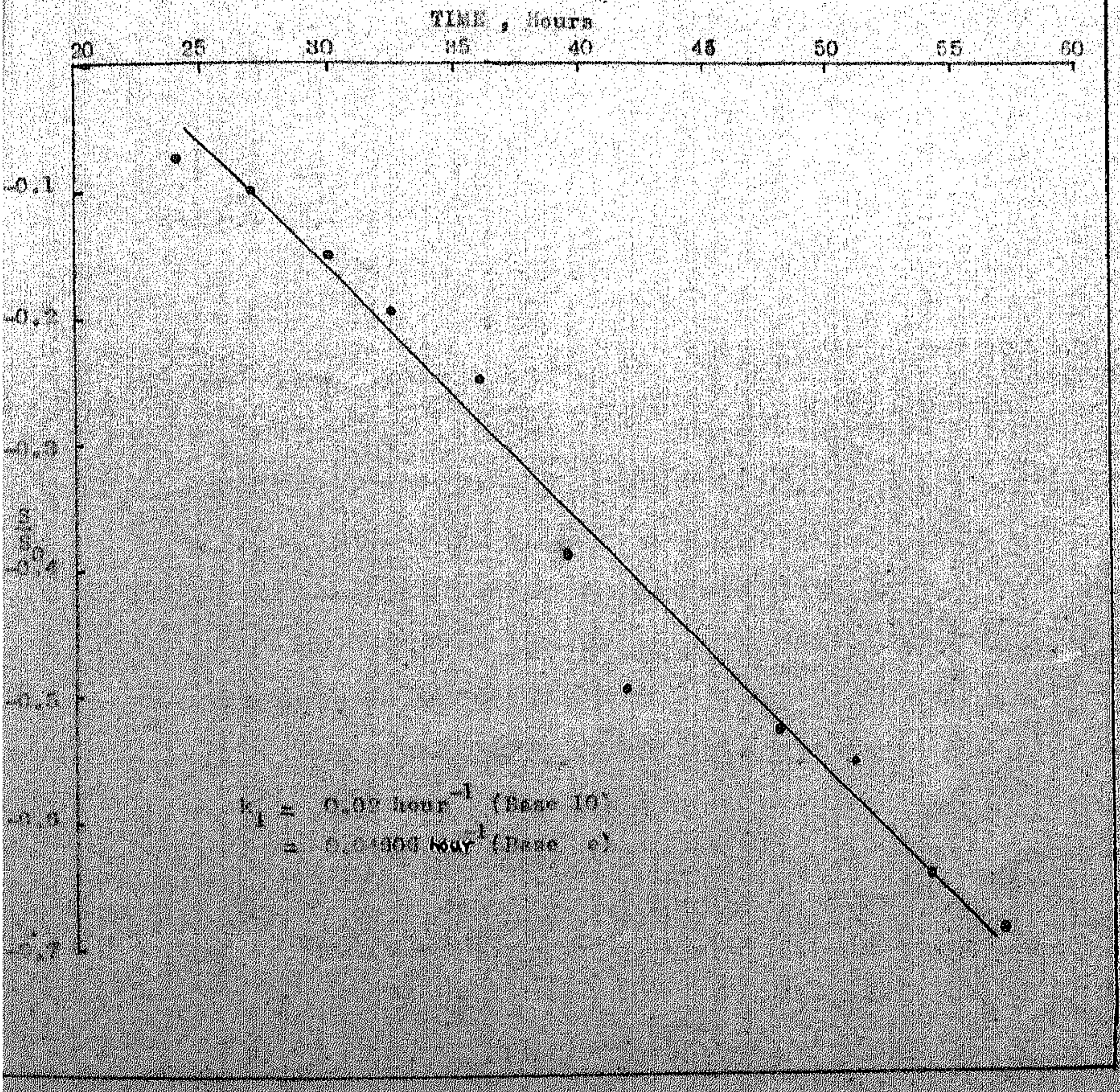

Figure 6 : CALCULATION OF [illegible] REACTION RATE CONSTANT
(Schroeder-Phelps Unimolecular Formulation)

Figure 7 : Evaluation of b for calculation of μ_{max}, K_s and k_x

Similarly from Figure 2b, the ultimate oxygen uptake of a microbial suspension of concentration 300 mg/l, comes out to be 395 mg/l. Therefore, the ultimate oxygen consumption of the microbial mass K" or dC/dx becomes 1.32 mg O_2/mg microbial mass. The slope of this line gives K_e as 5.07 day^{-1}, which corresponds to the autooxidation of the biomass at the rate of 93.7 percent per day, which is too high. Therefore for the purposes of the calculation of oxygen deficit by the rational model a value of K_e = 0.0514 day^{-1} and 0.162 day^{-1}, which corresponds to the autooxidation of 5% and 15% respictively biomass per day, has been used. This value is more realistic as it has been reported by Eckenfelder (31).

5.1.3 REAERATION RATE CONSTANT K_2

The data of the D.O. concentration with time, obtained as described in section 4.2.3.3 are plotted as log (C_s-C) against time as a straight time in Figure 3 . The slope of this lines gives the reaeration rate constant K_2 as:

Speed of the stirrer, rpm	30	50	70
Reaeration Rate constant K_2, day^{-1}, (base e)	4.146	7.909	12.16

5.2 SAG CURVES

As described in the section 4.1.4, the data for the D.O. profiles were obtained and plotted as D.O. deficit against time in Figures 8 to 12 for various initial microbial concentration to substrate concentration ratio. The sag curves as obtained from the Streeter - Phelps model and the rational model are also plotted in the same figures.

It is noted that for all cases the value of the critical time as given by the Streeter - Phelps first order model is

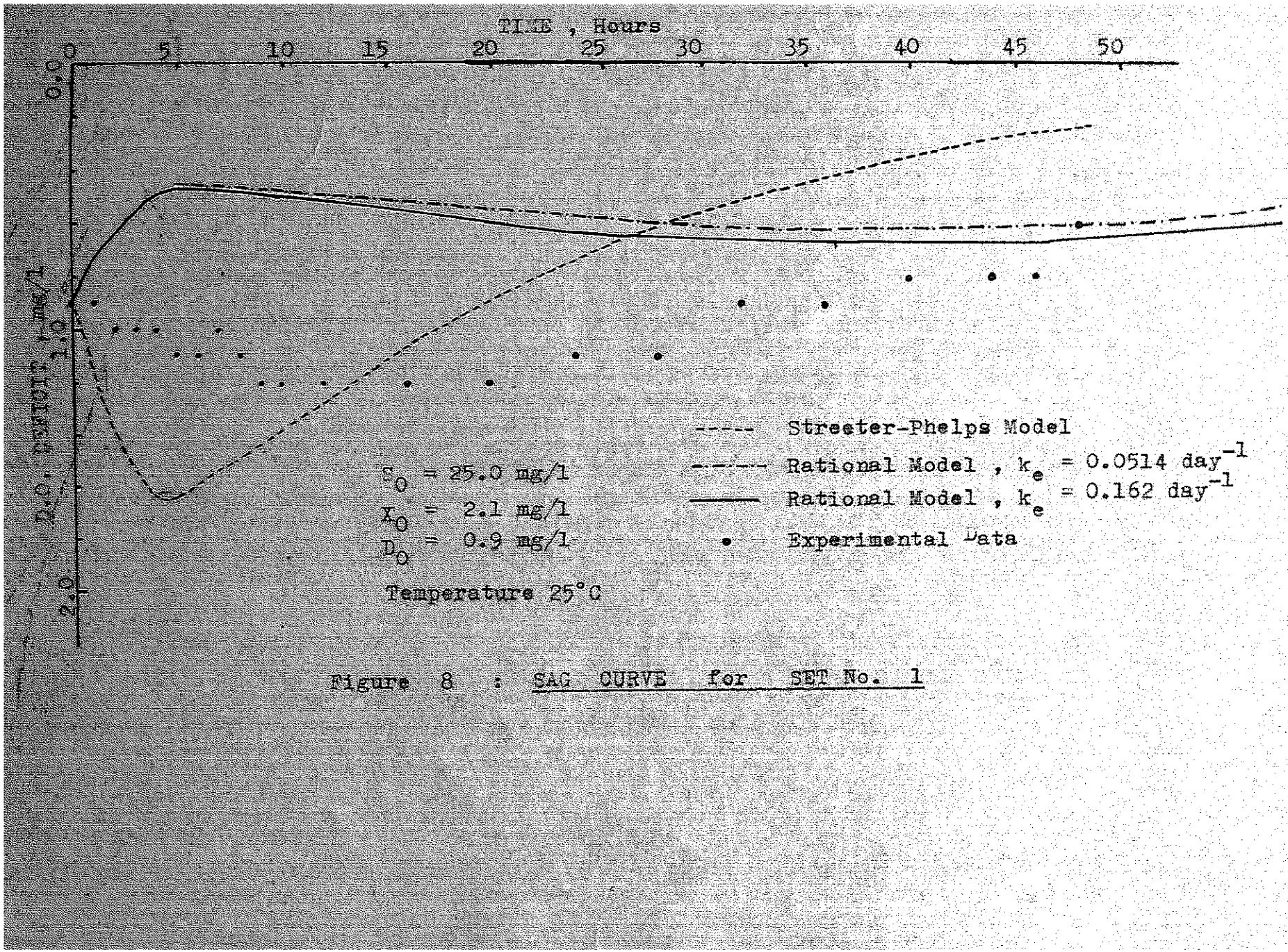

Figure 8 : SAG CURVE for SET No. 1

Time, Hours
0
4
8
12
16
20
24
28
32
36
40
44
0.0
0.1
L/m, Liters/mg
Streeter-Phelps Model
Rational Model, k_e = 0.054 day^{-1}
Rational Model, k_e = 0.162 day^{-1}
Experimental Data
L_0 = 26.0 mg/l
r_0 = 4.2 mg/l
D_0 = 0.9 mg/l
Temperature 25°C
Ca
Figure 9. BOD Curve for Ssr No. 2

Figure 10 : SAG curve for Set No. 3

Figure 11 : BOD CURVE for SET No. 4

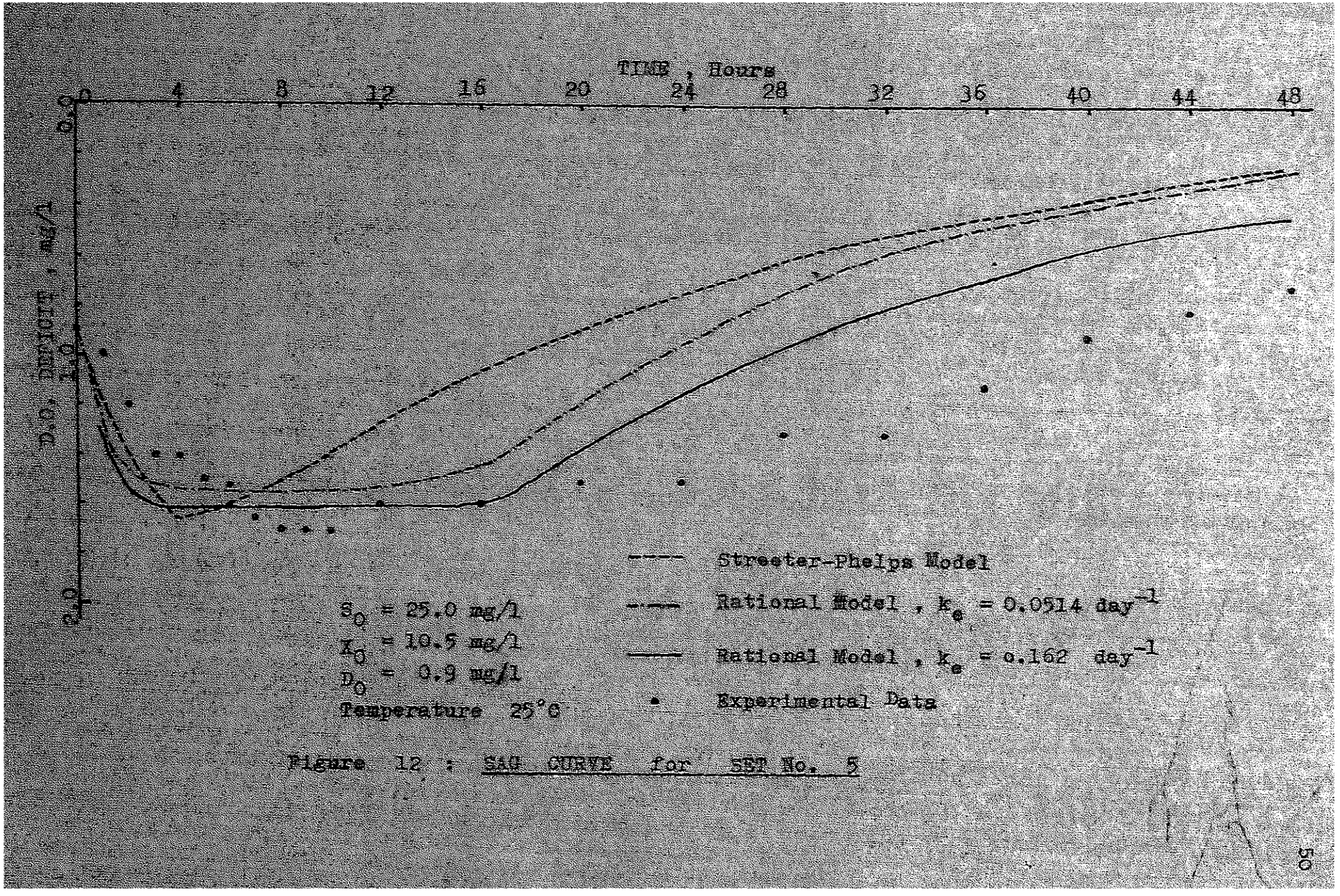

Figure 12 : SAG CURVE for SST No. 5

always less than the actually observed value and that of the critical deficit is always greater than the actually observed value. This will tend to predict higher critical D.O. deficit occuring earlier than the actual case. Hence any design of a wastewater treatment plant is likely to be over safe with this model, as it is likely to suggest a higher degree of the treatment, than is required from the point of view of the assimilating capacity of the stream for the pollution. Thus any design based on the Streeter - Phelps first order model is uneconomic, and a better approximation of the actual conditions can be acheived with the second order model proposed here.

The sag curves plotted in Figure 8 to 12 also show that as the substrate to microorganisms ratio is decreased we get more and more increase in D.O. deficit. This is obvious because with an increased number of microorganisms working on a substrate, the substrate will naturally be metabolised faster and in process B.O.D. will be exerted at a higher rate, causing increased deplection of D.O. content. This dependancy of the sag curve on microbial concentration also emphasises the impoitance of the microbial concentration for prediction of D.O. content in a water body.

The endogenous death rate as determined in the laboratory gave a value of K_e higher than what is usually encountered in biological systems, as described above in section 5.1.2. The values of the D.O. deficit from the rational model were calculated for values of K_e corresponding to the 5 and 15% antooxidation of the microbial mass per day, and are plotted in Figures 8 to 12 along with the sag curve as obtained

from the Streeter - Phelps model and also the experimental data. It is seen, that the higher rate of antooxidation gives a sag surve nearer to the experimental values. This means that in the stream models simulated in the laboratory the rate of endogenous respiration was higher than that generally present in a stream. On solving the equation 3.1.5 for higher values of K_e a better fitting sag curve to the experimental data may be obtained.

Similarly adjustment in the values of all other constants will produce a set a curves, which may be tried and fitted to the observed sag curve in any stream and thus the actual values of these constants existing in the stream may be approximated without setting up an experimentally simulated model of the stream in the laboratory. These constants then can be utilised in the design of a waste water treatment facility, discharging its effluent in the stream or can be put to some such other use. This gives us an indirect method of determination of these constants for a stream. This also adds to the flexibility of the model as there are seven of them and variation in every one will change the sag curve. Therefore, by trial and error almost any data observed in the nature can be filled to a curve and the constants determined for the prediction of D.O. downstream to wastewater out fall.

In Figures 8 and 9 we see that the D.O. deficit decreases a little in the beginning, as predicted by the rational model. This may be due to the higher rate of reaeration, due to the high value of deficit in the beginning;

which is more than the rate of deoxygenation thus offsetting it. As the time passes the D.O. deficit decreases and with it the rate of reaeration decreases too. A time comes when the rate of reaeration decreasses to the extent so as to become lower than the rate of deoxygenation, and the D.O. deficit again starts increasing. The D.O. deficit starts reducing once again when the rate of deoxygenatrion reduces, due to reduction in remaining B.O.D., sufficiently, so as to become lower than the rate of reaeration. The experimental data does not show the initial decreases in D.O. deficit. This could be due to a possibility of a mistake in measurement of the volume of stock suspension to produce such low microbial concentrations.

The sag curves as plotted in Figure 8 to Figure 12 show that for smaller values of t, the values of the oxygen deficit as obtained from the Streeter - Phelps Model and those from the rational Model vary significantly. But as is clear from Figure 12 , for higher values of initial microorganisms concentration, (x_o=10.5 mg/l) in the presence of lower substrate concentration (higher values of t) the two profiles agree with each other to a significant extent. This is in contrast to the fact that the Streeter - Phelps model disregards the microbial concentration while predicting the D.O. Actually as the time elapses, more and more substrate gets converted to microbial mass and therefore, for higher values of t, the time, the effect of the microbial concentration should be more pronounced. Therefore it can reasonably be expected that the data from the two models should differ significantly for smaller values of t and microbial concentration. Since as the time passes, substrate concentration

decreases and the microbial concentration decreases. It is possible that the substrate concentration becomes so small that it cases to have a significant effect, and the system essentially becomes a first order one, depending only on the microbial concentration. Thus although the Streeter - Phelps formulation is substrate concentration dependent and the rational Model becomes microbial concentration dependent for the higher values of t, both the expressions are the first order ones and hence show similar values.

As far as the actual values of the oxygen deficit are concerned we note that the experimental values are higher than those predicted by the rational model and are lower in the beginning and higher later than those given by the Streeter Phelps Model. This experimental data is also closer to the rational Model than the Streeter Phelps formulation. As a matter of fact the actual data is in agreement with the Streeter - Phelps valus only in a very small insignificant region where the two plots cross each other. At all other times the experimental values tally better with the rational Model rather than the classical Streeter - Phelps first order formulation, which is expected.

Unlike the results predicted by the Streeter - Phelps Model the critical conditions as predicted by the rational model are distributed over a relatively long duration of time, producing a sort of flat region in the curve. This again gives weightage to the importance of the microbial concentration. After a certain period of time enough biomass is produced to have a significant rate of respiration of its own. At the same time we have the older and dead microorganisms to be metabolised endogenously.

This conversion of the substrate into microbial mass does not change its effect on the D.O. content of the stream, as both are going to cause deoxygenation and hence maintain its rate. A balance is reached between the rate of deoxygenation and reoxygenation and the D.O. remains constant at that level for some time. When enough substrate and microbial mass has been completely oxidised to Co_2 and water, the phase of recovery stts and the rate of deoxygenation falls below the rate of reoxygenation causing the D.O. deficit to rise again.

The Streeter - Phelps equation, as it does not give any consideration to the concentration of the microbial mass, gives the same sag curve for all S/X ratios. It is clearly shown in Figures 8 to 12 that this is not so. The increasing microbial concentration causes higher D.O. deficits occuring earlier than in the case of lower microbial concentrations. This is also corroborated by the sag curves predicted by the rational model.

As the constants were determined at a different concentration of substrate and the microbial mass, it is quite likely that their values for the simulated stream are not the same as in the set up used for their determination. This perhaps accounts for the poor correlation of the experimental data with the rational model sag curves.

CHAPTER VI

CONCLUSIONS

The following conclusions are drawn from this study:

1. The Streeter - Phelps model is not adequate for the prediction of the sag curves due to the following reasons:

(a) The critical conditions as predicted by this model occur earlier and are more severe, than those observed experimentally. This will tend to produce oversafe designs for wastewater treatment plants.and hence will not be economically desirable.

(b) This model predicts that the sag curve remains the same for the same intial substrate concentration irrespective of the microbial concentration present in a stream. Experimental data shows that it is not so. As the microbial concentrations along the course of a stream are apt to vary significantly, depending upon the runoff and wastewater discharge received by it, any prediction of the D.O. deficit by the Streeter - Phelps model are likely to be erraneous. This discrepancy is taken care of in the rational model as different sag curves are predicted for different initial microbial concentrations.

2. The constants determined under conditions different than those in the simulated stream have caused the poor correlation of the experimental data to the sag curve predicted by the rational model. However the rational model still gives a better approximation to the experimental data as compared to Streeter Phelps model, showing that the metabolic process of the pollutants is a second order are rather than of first order. By a judicions choice of constants it will be possible to acheive a significant correlation in the experimental and rational model sag curves.

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APPENDIX - 'A'

A. 1 INTEGRATION OF EQUATION 3.6

Equation 3.6 is

$$\frac{dS}{dt} = - \mu_{max} \frac{S(A-S)}{K_s + S}$$

Seperating the variables we get,

$$\frac{K_s + S}{S(A-S)} \, dS = - \mu_{max} \, dt \quad \ldots\ldots \quad A.1.1$$

or, $$\left\{ \frac{K_s}{A} \cdot \frac{1}{S} + (1 + K_s/A) \cdot \frac{1}{A-S} \right\} dS = - \mu_{max} \, dt$$

Integrating from $S = S_o$ at $t = 0$ to $S = S$ at $t = t$ we get

$$\frac{K_s}{A} \ln (S/S_o) - (1 + K_s/A) \ln \frac{A-S}{A-S_o} = - \mu_{max} \, t \quad . \quad A.1.2$$

Therefore, $$t = \frac{1}{\mu_{max}} \ln \left\{ \left(\frac{A-S}{A-S_o}\right)^{1+K_s/A} \left(\frac{S_o}{S}\right)^{K_s/A} \right\}$$

or, $$t = \frac{1}{u_{max}} \ln \left\{ \left(\frac{A-S}{A-S_o} \cdot \frac{S_o}{S}\right)^{K_s/A} \frac{A-S}{A-S_o} \right\} \quad . \quad A.1.3$$

APPENDIX 'B'

B.1 EVALUATION OF CONSTANTS

B.1.1 K_x, K_s, μ_{max} and K'

Time, t hours	Microbial concentration, x mg/l	Substrate concentration as C.O.D. mg/l
0	8	440
5	12	430
9	13.5	430
13	13.5	430
16	20	400
24	27.5	370
27	38	350
30	55	210
32.5	63	280
36	84	250
39	94	180
42	107	140
48	115	130
51	122	110
54	134	100
57	140	90
60	150	100
66	153	80
72	158	80

B. 1.2 DETERMINATION OF K', K" AND K_o ON WARBURG RESPIROMETER

B.1..2.1 DETERMINATION OF FLASK CONSTANTS

Temperature = 25°C

P_o = 10,000 mm of Brodie's fluid

= 0.0283

V_f = 2.6 ml = 2600 µl

Flask No.	V_g, ml	Flask constant K, l/mm
1	14.2	1.56
2	18.86	2.06
3	16.38	1.79

Since, x = Kh in µl of oxygen consumed at

$$= \frac{32}{22.4V}^{NTP} \text{ Kh in mg/l of substrate}$$

= 0.55 Kh

where, V = volume substrate, ml

B.1.2.2 OXYGEN UPTAKE DATA

Time, t minutes	Oxygen uptake for glucose mg/l	Oxygen uptotake for microorganism under endogenous conditions mg/l
30	46.3	12.6
60	103.0	56.5
90	166.2	73.0
120	220.0	100.0
150	254.0	115.0
180	272.0	124.5
210	301.0	139.0
240	322.0	151.0
270	342.0	151.0
300	366.0	176.0
330	384.0	188.0
360	405.0	214.0
390	432.0	228.5
420	456.0	246.0
450	476.0	262.5
480	494.0	273.5
510	506.0	284.0
540	542.0	300.0

B.1.3 EVALUATION OF K_2, THE REAERATION RATE CONSTANT

Temperature = $22^{o}C$

C_s = 8.8 mg/l

Vol. of water = 2.5 l

Vessel used : 30 cm. x 10 cm ø cylindrical jar

TIME, minute	D.O. concentration, mg/l		
	30 rpm	50 rpm	70 rpm
0	1.94	3.22	5.00
10	2.18	3.54	5.47
20	2.35	3.85	5.63
30	2.57	4.10	5.87
40	2.89	4.25	6.10
50	3.05	4.50	6.27
60	-	4.82	6.45
70	-	5.00	6.70

B.2 DATA FOR SAG CURVES

B. 2.1 EXPERIMENTAL VALUES

Time, hrs.	Oxygen Deficit, mg/l				
	Set No.1 x_o=2.1 mg/l	Set No.2 x_o=4.2 mg/l	Set No.3 x_o=6.3 mg/l	Set No.4 x_o=8.4 mg/l	Set No. 5 x_o=10.5 mg/l
0	0.9	0.9	0.9	0.9	0.9
1	0.90	0.95	0.95	1.0	1.0
2	1.0	0.95	0.95	1.0	1.2
3	1.0	1.0	1.0	1.1	1.4
4	1.0	1.1	1.0	1.15	1.4
5	1.10	1.1	1.1	1.15	1.5
6	1.10	1.1	1.15	1.1	1.6
7	1.0	1.15	1.20	1.2	1.65
8	1.10	1.2	1.2	1.25	1.7
9	1.2	1.2	1.3	1.3	1.7
10	1.2	1.25	1.3	1.3	1.7
12	1.2	1.2	1.25	1.4	1.6
16	1.2	1.25	1.25	1.4	1.6
20	1.2	1.3	1.2	1.3	1.5
24	1.10	1.3	1.1	1.2	1.5
28	1.10	1.2	1.1	1.15	1.3
32	0.90	1.1	0.95	1.0	1.3
36	0.90	1.0	0.90	1.0	1.1
40	0.8	1.0	0.8	1.0	0.9
44	0.8	0.9	0.8	0.9	0.8
48	0.6	0.8	0.8	0.9	0.7

3.2.2 SAG CURVE BY RATIONAL MODEL

3.2.2.1 VALUES FOR K_0 = 0.0514 day^{-1}

S	x_o=2.1 mg/l		4.2 mg/l		6.3 mg/l		8.4 mg/l		10.5 mg/l	
mg/l	t hrs	D mg/l	t hrs	D mg/l	t hrs	D mg/l	t hrs	D mg/l	t hrs	D mg/l
15.0	0	0.9	0	0.9	0	0.9	0	0.9	0	0.9
14.0	4.57	0.456	2.38	0.824	1.61	1.012	1.21	1.1651	0.978	1.265
13.0	8.65	0.452	4.66	0.828	3.19	1.023	2.42	1.2883	1.96	1.48
12.0	12.37	0.480	6.86	0.831	4.75	1.033	3.64	1.2883	2.95	1.5325
11.0	15.83	0.511	9.00	0.833	6.31	1.0441	4.85	1.2881	3.95	1.5317
10.0	19.09	0.539	11.10	0.835	7.85	1.0442	6.08	1.287	4.96	1.5307
9.0	21.19	0.562	13.17	0.836	9.40	1.0440	7.32	1.286	5.99	1.5293
8.0	25.19	0.580	15.22	0.837	10.96	1.0435	8.58	1.285	7.05	1.527
7.0	28.10	0.592	17.26	0.837	12.54	1.0426	9.86	1.284	8.31	1.525
6.0	30.97	0.604	19.32	0.836	14.14	1.0414	11.17	1.282	9.24	1.523
5.0	33.81	0.610	21.39	0.835	15.77	1.039	12.52	1.279	10.39	1.520
4.0	36.65	0.6099	23.51	0.834	17.45	1.037	13.91	1.276	11.58	1.517
3.0	39.52	0.609	25.67	0.832	19.19	1.034	15.39	1.273	12.82	1.513
2.0	42.43	0.608	27.90	0.829	21.00	1.031	16.88	1.269	14.13	1.508
1.0	45.43	0.605	30.22	0.826	22.89	1.026	18.48	1.264	15.52	1.502
0.0	48.54	0.602	32.66	0.806	24.89	0.992	20.18	1.188	17.00	1.399
9.0	51.82	0.592	35.25	0.757	27.04	6.923	22.01	1.105	18.59	1.289
8.0	55.29	0.556	38.03	0.704	29.35	0.850	23.99	1.007	20.32	1.165
7.0	59.06	0.511	41.06	0.640	31.89	0.773	26.18	6.909	22.24	1.051
6.0	63.21	0.464	44.44	0.576	34.74	0.693	28.6	0.813	24.4	0.9373
5.0	67.92	0.412	48.29	0.509	38.0	0.692	31.47	0.712	26.90	0.818
4.0	73.45	0.355	52.85	0.435	31.88	0.518	34.84	0.604	29.89	0.692
3.0	80.29	0.291	58.58	0.355	36.73	0.420	39.08	0.488	33.65	0.557
2.0	89.57	0.220	66.28	0.266	53.38	0.314	44.90	0.362	38.83	0.413

B.2.2.2 VALUES FOR K_o = 0.162 day^{-1}

Substrate concentration. S, mg/l	x_o = 2.1 mg/l		x_o=4.2 mg/l		x_o=6.3 mg/l		x_o= 8.4 mg/l		x_o=10.5 mg/l	
	t hrs	D mg/l	t hrs	D mg/l	t hrs	D mg/l	t hrs	D mg/l	t hrs	D mg/l
25.0	0	0.9	0	0.9	0	0.9	0	0.9	0	0.9
24.0	4.57	0.476	2.38	0.859	1.61	1.056	1.22	1.20	0.98	1.305
23.0	8.65	0.475	4.66	0.86	3.19	1.087	2.42	1.371	1.96	1.552
22.0	12.37	0.508	6.86	0.867	4.75	1.099	3.64	1.371	2.95	1.620
21.0	15.83	0.546	9.00	0.869	6.31	1.110	4.85	1.371	3.95	1.619
20.0	19.09	0.576	11.10	0.871	7.85	1.121	6.08	1.370	4.96	1.619
19.0	22.10	0.600	13.17	0.872	9.40	1.121	7.32	1.370	5.99	1.617
18.0	25.19	0.624	15.22	0.874	10.96	1.121	8.58	1.369	7.05	1.616
17.0	28.10	0.643	17.26	0.882	12.54	1.121	9.86	1.368	8.13	1.614
16.0	30.9	0.656	19.32	0.881	14.14	1.119	11.17	1.366	9.24	1.612
15.0	33.81	0.663	21.39	0.881	15.77	1.117	12.52	1.364	10.39	1.610
14.0	36.65	0.664	23.51	0.880	17.45	1.115	13.91	1.362	11.58	1.607
13.0	39.52	0.663	25.67	0.878	19.19	1.113	15.36	1.358	12.82	1.603
12.0	42.43	0.662	27.90	0.876	21.00	1.110	16.88	1.355	14.13	1.599
11.0	45.43	0.661	30.22	0.874	22.89	1.106	18.48	1.350	15.52	1.594
10.0	48.45	0.658	32.66	0.869	24.89	1.101	20.18	1.344	17.00	1.572
9.0	51.81	0.654	35.25	0.864	27.04	1.054	22.01	1.252	18.59	1.468
8.0	55.29	0.643	38.03	0.811	29.35	0.989	23.99	1.164	20.32	1.348
7.0	59.06	0.604	41.06	0.753	31.89	0.913	26.18	1.069	22.24	1.227
6.0	63.2	0.559	44.44	0.692	34.74	0.826	28.64	0.964	24.40	1.108
5.0	67.92	0.506	48.29	0.621	38.00	0.741	31.47	0.864	26.90	0.989
4.0	73.45	0.451	52.85	0.550	41.88	0.653	34.84	0.758	29.89	0.867
3.0	80.29	0.391	58.53	0.474	46.73	0.559	39.08	0.646	33.65	0.73
2.0	89.57	0.323	66.28	0.389	53.38	0.456	44.90	0.525	38.83	0.59

B. 2.3. SAG CURVE BY STREETER - PHELPS MODEL

$K_1 = 0.04606\ hr^{-1}$

$K_2 = 12.16\ day^{-1} = 0.507\ hr^{-1}$

$S_o = 0.9\ mg/l$

Time, t hours	D.O. Deficit mg/l
0	0.9
4	1.658
4.08	1.775 (Critical values)
8	1.496
12	1.262
16	1.050
20	0.870
24	0.729
28	0.605
32	0.505
36	0.420
40	0.349
44	0.292
48	0.241

APPENDIX 'C'

FORTRAN IV (IBM 7044/1401 VERSION) PROGRAM FOR THE SOLUTION OF THE EQUATION 3.1.5, BY RUNGE-KUTTA (FOURTH ORDER) METHOD.

```
      DIMENSION AKAY(10)
      F(S,D)=C*(AKS+S)*D/(S*(A-S))-(AKDAS+B*(AKS+S)/S)
      READ101,AKX,AKS,AKMAX,AK2,AKDAS,AKE,DCDX
  101 FORMAT(7F10.4)
      PRINT113,AKX,AKS,AKMAX,AK2,AKDAS,AKE,DCDX
  113 FORMAT(X,3HKX=F8.3,5X,3HKS=F8.3,5X,5HKMAX=F9.4/X,3HK2=F8.3,3X,5HKD
     1AS=F8.3,7X,3HKE=F8.3,5X,6HDC/DX=F8.3)
      READ102,DEL,EPS,ITER,JSETS
  102 FORMAT(2F8.3,2I4)
      PRINT114,DEL,EPS,ITER,JSETS
  114 FORMAT(X,4HDEL=F8.3,5X,4HEPS=F8.3,5X,19HITERATIONS ALLOWED=I4,5X,5
     1HSETS=I4)
      B=(AKE*DCDX)/(AKX*AKMAX)
      C=AK2/AKMAX
      DO 8 L=1,JSETS
      PRINT103
      PRINT104
      PRINT103
  103 FORMAT(X,14(1H-))
  104 FORMAT(X,14HNEW SET BEGINS)
      READ105,S0,X0,D0,H,SMIN
  105 FORMAT(5F8.3)
      A=AKX*X0+S0
      PRINT106,S0,X0,D0,H,SMIN
  106 FORMAT(X,3HS0=F8.3,3X,3HX0=F8.3,3X,3HD0=F8.3,3X,2HH=F8.3,3X,5HSMIN
     1=F8.3)
      INTER=(S0-SMIN)/(-DEL)+1.
      D=D0
      PRINT107,INTER
  107 FORMAT(X,10HINTERVALS=I6)
      PRINT112
      PRINT109
      PRINT112
```

.....Contd.

```
109 FORMAT(3X,1HI,4X,9HS IN MG/L,4X,13HTIME IN HOURS,1X,15HDEFICIT IN
   1MG/L,1X,16HERROR IN DEFICIT)
112 FORMAT(X,65(1H*)/)
    DO 7 I=1,INTER
    AI=I
    S=S0+AI*DEL
  1 AKAY1=H*F(S,D)
    AKAY2=H*(F(S+H/2.,D+AKAY1/2.))
    AKAY3=H*F(S+H/2.,D+AKAY2/2.)
    AKAY4=H*F(S+H,D+AKAY3)
    CORR=(AKAY1+2.*(AKAY2+AKAY3)+AKAY4)/6.
    DNEW=D+CORR
    IF(DNEW)10,9,9
 10 PRINT115
115 FORMAT(X,31HOXYGEN DEFICIT BECOMES NEGATIVE)
  9 ERROR=(DNEW-D)/DNEW
    IF(ABS(ERROR)-EPS)11,11,3
  3 D=DNEW
  5 CONTINUE
    CALCULATIONS FOR 'T', GIVEN'S'
 11 AS=A-S
    AS0=A-S0
    X1=ALOG(S0)-ALOG(S)
    X2=ALOG(AS)-ALOG(AS0)
    T=(((AKS/A+1.)*X2+(AKS/A)*X1)/AKMAX)*24.
    PRINT111,I,S,T,DNEW,ERROR
111 FORMAT(X,I3,2X,4(E13.6,2X))
    IF(DNEW-EPS)8,8,7
  7 CONTINUE
  8 CONTINUE
    STOP
    END
```